

Synthesis and characterization of polycrystalline Sn and SnO₂ films with wire morphologies

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Abstract

A new electrodeposition condition has been developed to prepare films composed of Sn wires, using dimethyl sulfoxide (DMSO) as a plating medium. The morphology of Sn deposits varied significantly depending on the aging time of the solution as well as the amount of electric charge passed through the cell prior to deposition. The wire morphology was obtained only when the DMSO solution containing 0.1 M SnCl₂ and 0.5 M NaNO₃ was aged for 2 weeks at room temperature and 20 C of electric charge were passed through the cell (−1.8 V vs. Ag/AgCl at the working electrode) before deposition. Otherwise, spherical agglomerations of Sn particles that resemble the shape of cauliflowers were obtained. Electrospray ionization mass spectrometry revealed that the combination of the aging and passing electric charge processes increased the amount of tetravalent tin ions and the chloride to tin ratio in the plating medium, resulting in the formation of SnCl₆^{2−} species without which Sn wires cannot be formed. The electrochemically deposited Sn films were converted to SnO₂ films by thermal oxidation while preserving the original morphologies. The SnO₂ films with wire morphology exhibited superior photoelectrochemical performances compared to the cauliflower morphology although both of these morphologies contain SnO₂ nanoparticles of similar sizes (6–15 nm). Optimizing conditions to control the fine details of wire growth is expected to create opportunities to investigate and exploit wire morphologies of Sn and SnO₂ to construct efficient and cost-effective electrode materials for Li-ion batteries and photoelectrochemical cells.

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1. Introduction

Sn and SnO₂ have received great attention for application in energy production/storage devices. Both Sn and SnO₂ are recognized as high capacity anode materials for Li-ion batteries, while SnO₂ has also been extensively studied for photocatalytic and photoelectrochemical applications [1–4]. The bandgap of SnO₂ ($E_g = 3.6$ eV) is too large to utilize the visible portion of the solar spectrum, but its low lying conduction band makes it possible to efficiently accept photogenerated electrons from other semiconductors when used in multi-component systems (i.e.

SnO₂/ZnO, SnO₂/TiO₂), which can significantly reduce the rate of electron-hole recombination [4].

The efficiencies of Sn and SnO₂ electrodes in these applications are largely dependent on their nano- and micro-scale interfacial structures [5–7]. These structures not only determine the surface areas available for electrochemical and photoelectrochemical reactions but also affect the overall charge transport properties of the electrodes. Among various polycrystalline morphologies, the wire morphology is of strategic importance for photoelectrochemical applications, because its one-dimensional architecture can minimize the randomness of the charge carriers' pathway and achieve superior charge transport properties when compared to other polycrystalline morphologies of equal surface areas [8,9]. When doped with indium or fluorine, SnO₂ films with wire morphology

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may serve as high surface area conducting substrates for the construction of photoelectrochemical and photovoltaic devices.

Here, we report a new electrochemical condition to prepare Sn films with wire morphology that does not require soft or hard templates. Previously, electrodeposition of Sn and SnO₂ has been mainly carried out using aqueous media, which are not chemically stable over time as they generate undesirable precipitates of tin hydroxides in solution [10,11]. In this study, we explored the possibility of using dimethyl sulfoxide (DMSO) as a plating medium to electrodeposit Sn films. We discovered that adopting non-aqueous DMSO media not only eliminates the precipitation of tin hydroxides, but also provides a new reaction environment to create a highly desirable wire morphology in Sn films. These films can be converted to SnO₂ films by thermal oxidation while still preserving the wire morphology that exhibited significantly enhanced photoelectrochemical properties compared to other morphology.

The purpose of this communication is twofold. One is to report a new and rare electrochemical condition to construct and exploit wire morphologies of Sn and SnO₂ using a DMSO medium. The other is to discuss a few experimental factors in electrodeposition that can be easily overlooked but have a significant impact on morphology of deposits (e.g. repeated usage of plating solution, aging of plating solution, gas bubbling during deposition). Although our current understanding of these factors for Sn–DMSO media are far from complete due to their intrinsic complexity, this study will provide useful insights to the understanding and designing of electrochemical conditions to achieve and reproduce desired morphologies.

2. Experimental

Sn films were deposited potentiostatically at room temperature, using a conventional three-electrode set-up in an undivided cell (Princeton Applied Research VMP2 Multi-channel Potentiostat/Galvanostat). The plating medium was a 50 mL DMSO solution containing 0.1 M SnCl₂ and 0.5 M NaNO₃ as the source of tin ions and the supporting electrolyte, respectively. A stainless steel foil was used as the working electrode (WE) while the counter electrode (CE) was prepared by sputter coating a 250 Å thick titanium layer, followed by a 500 Å thick platinum layer on clean glass slides. Cathodic depositions of Sn were carried out by polarizing the WE at –1.8 V versus a Ag/AgCl in 4 M KCl reference electrode.

SnO₂ films were prepared by thermally oxidizing the electrodeposited Sn films with the cauliflower and wire morphologies at 550 °C for 90 min in air. The SnO₂ films produced in this way retained the original Sn morphologies.

X-ray diffraction patterns were obtained using copper K α radiation (Scintag X2 Powder X-Ray Diffractometer), which confirmed the purity and crystallinity of both Sn and SnO₂ films. Morphologies of the deposited films were

studied by Scanning Electron Microscopy (Jeol JSM 840) and Field Emission Scanning Electron Microscopy (FEI Nova NanoSEM 200).

Electrospray Ionization Mass Spectrometry (ESI-MS) was employed to analyze Sn-containing species in DMSO solutions at various stages. All electrospray ionization analyses were carried out using a FinniganMAT LCQ Classic (ThermoElectron Corp) mass spectrometer. The electrospray needle voltage was set at 4.5 kV, the heated capillary voltage was set to 10 V and the capillary temperature 220 °C. Typical background source pressure was 1.3×10^{-5} Torr as read by an ion gauge. The sample flow rate was approximately 8 μ L per minute. The drying gas was nitrogen. The LCQ was scanned to 1000 amu for these experiments. The sample was dissolved in acetonitrile and water.

The photoelectrochemical properties of the SnO₂ electrodes were characterized by measuring the photocurrent at zero bias (short circuit current). The electrolyte used was 40 mL of a 0.02 M NaOH aqueous solution purged with argon for 30 min before measuring. The light source was a 300 W Xenon arc lamp with a light intensity of 772 mW/cm². The recorded photocurrent values were normalized to the masses of the individual electrodeposits to eliminate the effect of different amount of electrodeposits in each sample.

3. Results and discussion

Fig. 1a and b show Scanning Electron Microscopy (SEM) images of Sn films deposited from a freshly prepared DMSO solution containing 0.1 M SnCl₂ and 0.5 M NaNO₃. The Sn deposits are composed of spherical agglomerations of particles that resemble the shape of cauliflowers. The size of individual Sn particles ranges from 6 to 15 nm. When the same plating solution is used repeatedly to deposit more Sn films, the morphology of the films changes drastically from cauliflowers to wires, after approximately 20 C are passed through the cell (Fig. 1c). These films contain 400–600 nm thick Sn wires that are entangled together forming root-like structures.

In order to probe a possibility of depositing SnO or SnO₂ films from a DMSO medium, we introduced oxygen gas to the plating medium before and during deposition. Dissolved oxygen may be able to oxidize Sn²⁺ ions to Sn⁴⁺ ions in the plating medium, and it can also be involved with electrochemical reaction generating OH⁻ ions ($O_2 + H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$) [11,12]. Electrochemical generation of OH⁻ ions increases the local pH near the WE affecting the solubility of metal ions, and has been used as a main mechanism to deposit various oxide films [12]. When the plating medium was saturated with oxygen gas before electrodeposition, we observed no apparent effect on the composition or morphology of Sn films deposited. However, when oxygen gas was introduced near the WE during the electrodeposition process, an interesting morphological change was observed: Sn wires grew more

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